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Geochemical and Biogeochemical Exploration of Molybdenum-Copper Mineralization at Setting Net Lake

District of Kenora (Patricia Portion)

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By
W. D. Wolfe

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ABSTRACT

A study of the effectiveness of geochemical and biogeochemical exploration methods in detecting low-grade 'porphyry-type' molybdenum-copper mineralization in glaciated Precambrian terrain was carried out in 1971 near Setting Net Lake, northwestern Ontario. An extensive zone of molybdenite concentration has been outlined and described by Ayres (1968; 1969a,b) and Ayres and Averill (1971) in the northern part of a small (5.7 km^2) (2.2 square miles) epizonal pluton of equigranular to porphyritic granodiorite and quartz monzonite that intruded Archean mafic metavolcanics and metasediments at the northeastern end of Setting Net Lake. Within an east-trending mineralized zone that is up to 450 m (1,500 feet) wide and 2400 m (8,000 feet) long, widespread molybdenite has been found. It occurs along the margins of narrow, variably spaced quartz veins that fill joints in the stock, and as minor disseminated mineralization throughout the granodiorite and quartz monzonite. The mineralized zone also contains pyrite and minor chalcopyrite.

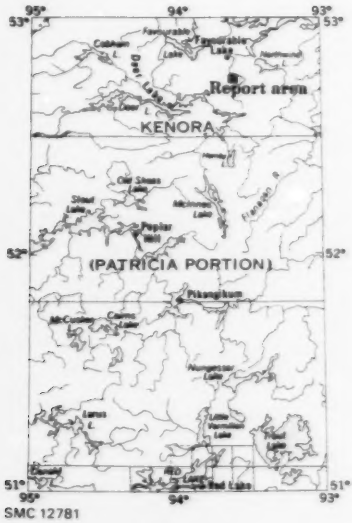

Figure 1

Key map showing location of area studied.

Average metal abundances estimated from analyses of 100 rock samples collected from 50 outcrop sites within the Setting Net Lake stock are (in ppm): Cu-8, Mo-1.7, Zn-30, Mn-277 in the unmineralized south half of the stock, and Cu-61, Mo-26, Zn-30, Mn-240 in the mineralized north half of the stock.

The Setting Net Lake area lies in the region that was covered by glacial Lake Agassiz during retreat of the Wisconsin ice front into northwestern Ontario. It is partly covered by massive to varved, calcareous Pleistocene lake clays. The explored zone of mineralization occurs mainly on a thinly drift-covered bedrock topographic high surrounded by extensive poorly-drained spruce swamp and muskeg resting on clay deposits of variable thickness. Well differentiated podzolic soils are developed on well-drained, sandy stone tills that mantle the upland areas.

Molybdenum concentrations range from 1 ppm to 80 ppm in 'B' horizon soils and from 2 ppm to 71 ppm in the ash of second year black spruce needles. Patterns of anomalously high molybdenum in 'B' horizon soils are restricted to bedrock-glacial till 'windows' in the clay-swamp cover. Within a relatively restricted area, soil pH ranges from 4.5 near oxidizing sulphides to 7.5 over calcareous Pleistocene clays. Soil samples are difficult to obtain in areas of thick organic accumulation and molybdenum is not precipitated in the alkaline soils developed on clay deposits.

The pattern of anomalously high molybdenum in second year black spruce needles extends into both the clay and swamp environments and is more widespread and sharply defined than the corresponding soil anomaly. The molybdenum content of vegetation may be regarded as an indirect indicator of Mo levels in soil solution, and the existence of anomalous Mo in trees growing in alkaline soil environments confirms pH-solubility relationships which predict increased solubility (i.e. mobility) of the molybdate $(MoO_4)^{-2}$ ion with increasing pH.

Copper concentrations range from 3 ppm to 311 ppm in 'B' horizon soils and from 32 ppm to 322 ppm in the ash of second year black spruce needles. The pattern of anomalous copper distribution in 'B' horizon soil is strongly localized at the eastern end of the mineralized zone and is generally less widespread than the molybdenum pattern. Anomalous copper levels extend into areas of high pH soils developed on clays and apparently reflect precipitation of laterally transported copper in the high pH environment.

GEOCHEMICAL AND BIOGEOCHEMICAL EXPLORATION OF MOLYBDENUM-COPPER MINERALIZATION AT SETTING NET LAKE DISTRICT OF KENORA (PATRICIA PORTION)

By

W.J. Wolfe[1]

INTRODUCTION

LOCATION AND ACCESS

Setting Net Lake is about 195 km (120 miles) north of Red Lake, the closest road terminus, and is accessible only by float- or ski-equipped aircraft (see key map, Figure 1). The Indian settlement of Sandy Lake is 30 km (20 miles) north-northeast of Setting Net Lake. The granodiorite-quartz monzonite pluton discussed in this report occupies about 5.7 km^2 (2.2 square miles) and is centred 1.6 km (1 mile) northeast of the north end of Setting Net Lake at Latitude 52°48' and Longitude 93°35'. Several trails, surveyed baselines, and picket lines provide excellent access to the area underlain by the intrusion.

SCOPE AND PURPOSE OF THE GEOCHEMICAL SURVEY

The Setting Net Lake geochemistry field project was primarily designed to test the use of surface geochemical and biogeochemical exploration methods in an area of widespread, low-grade Precambrian molybdenite-pyrite-chalcopyrite mineralization that is covered by extensive transported Quaternary overburden including variable thicknesses of boulder till and Late Pleistocene lake clay. The effectiveness of the methods was determined by the detection of anomalous concentrations of trace elements (mainly Mo and Cu) in rocks, soils, and vegetation, and by relating the anomalous halos to the occurrence of known molybdenite mineralization in the northern part of the Setting Net Lake pluton.

Recent studies by Warren and Delavault (1965), Hornbrook (1969; 1970), and Canney (1970; 1971) have illustrated examples of substantial molybdenum accumulation in the needles and twigs of coniferous vegetation (balsam fir, white spruce, lodgepole pine, alpine fir) rooted in soils developed over low grade molybdenum-copper deposits in British Columbia and Maine. For this reason, the present geochemical survey included a study of Mo and

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Cu distribution in certain widespread species of vegetation common to the Precambrian Shield of Ontario.

Geochemical and biogeochemical studies over mineralized and barren parts of the Setting Net Lake pluton were directed toward the detection of anomalous patterns of primary Mo and Cu distribution within the pluton and the identification of anomalous secondary dispersion patterns in the surface environment. One hundred samples of bedrock were collected from 50 outcrop sites within the boundaries of the pluton according to a paired system of duplicate sampling used to compare local sampling variability at the outcrop level with overall variability within the intrusion. Samples of 'B' horizon soil were collected at intervals of 130 m (400 feet) on a grid system covering the main zone of Mo mineralization. Samples of lower bark, second year twigs, and second year needles were collected from black spruce (*Picea mariana*) at 25 sites near known mineralization and in surrounding terrain covered by Pleistocene glacial lake clay. Similar samples were collected from 5 control sites in the barren southern part of the intrusion. At selected sites, samples of lower bark and second year twigs were also collected from jack pine (*Pinus banksiana*), trembling aspen (*Populus tremuloides*) and white birch (*Betula papyrifera*) for purposes of comparing Mo and Cu levels in the various plant species. Samples of primary and oxidized ore were collected for mineralogical studies and pH measurements were made in streams, swamps and soils near oxidizing sulphide mineralization. Samples of rocks, soil and plant material were analyzed for Cu, Pb, Zn, Mo, and Mn.

ACKNOWLEDGMENTS

The writer was assisted in the field collection, subsampling and preparation of geochemical and biogeochemical samples by L.B. Owen, M.J. Shulist and W.R. Alemayehu. Much of the background information contained in this report concerning the geology and mineral deposits of the area and the mineralogy of the stock, is attributable to L.D. Ayres of the geological staff of the Division of Mines, Ministry of Natural Resources. All chemical analyses were performed by the staff of the Mineral Research Branch of the Division of Mines under the direction of A.E. Pitts.

GEOLOGY

REGIONAL GEOLOGY

The geology of the Setting Net Lake area has been previously described by Ayres (1968; 1969a,b; 1970), and the general geological summary that follows is intended only to provide a background for presentation of the geochemical data. Ontario Department of Mines Preliminary Map P.538 should be examined for additional information concerning the geology and mineral deposits of the area.

The molybdenum-bearing, porphyritic granitic pluton which is the subject of this report, was emplaced in a south-southeast-trending, Early Pre-

cambrian, metavolcanic-metasedimentary belt that extends from Northwind Lake to west of the Ontario—Manitoba boundary. The greenstone belt is bordered by composite granitic batholiths and is at least 11 km (7 miles) wide in the area between Setting Net and Northwind Lakes. The metavolcanic-metasedimentary sequence is at least 6000 m (20,000 feet) thick and is composed predominantly of pillowed to massive, locally variolitic mafic flows and coeval metagabbro-metadiorite intrusions, but felsic to intermediate flows and pyroclastic rocks are locally abundant, especially west of Northwind Lake. Volcaniclastic greywacke and siltstone form several, relatively thin formations in the sequence. Minor occurrences of conglomerate, slate, chert, ferruginous chert, iron formation and marble are also found. Metamorphic grade ranges from middle greenschist in the centre of the belt to middle almandine-amphibolite and hornblende-hornfels facies adjacent to the large batholithic masses that border on the greenstone belt. A narrow hornblende-hornfels aureole has developed about the Setting Net Lake pluton.

The metavolcanic-metasedimentary sequence has been folded about axes trending southeast, parallel to the boundaries of the belt. Local east-trending cross folds are also present. Numerous faults have been recognized in the area but two major systems are particularly important: (1) southeast-trending faults that have large components of vertical movement with the southwest side having moved up, and (2) south- to southeast-trending faults with right-hand strike separation. Ayres (1969a) has noted that some of these faults were a major control for the localization of copper mineralization.

The Setting Net Lake pluton is a small, oval, epizonal stock of equigranular to porphyritic granodiorite and quartz monzonite that intruded Archean mafic metavolcanics and metasediments near the north end of Setting Net Lake. The granodiorite has sharp, chilled contacts against hornfelsed mafic volcanic country rocks; the narrow contact metamorphic aureole is best observed along the northern margin of the stock. Porphyritic facies of the stock contain coarse-grained microcline, quartz and minor plagioclase phenocrysts in a fine- to medium-grained, leucocratic groundmass that has less than 4 percent biotite (Ayres and Averill 1971). Microcline phenocrysts form up to 10 percent of the northeastern part of the stock, but are much less abundant in the southern and eastern parts of the intrusion. Aplite dikes are widespread in the stock, but narrow and irregular pegmatite veins are rare and are localized in the south-central part of the body. Low grade regional metamorphism has produced partial recrystallization of the granodiorite and quartz monzonite and partial alteration of oligocalse to albite (Ayres and Averill 1971).

PLEISTOCENE GEOLOGY, TOPOGRAPHY, AND PHYSICAL FEATURES

During the Wisconsin glaciation, the Setting Net Lake area was entirely overridden by a fan-shaped advance of continental ice that formed part of a major ice lobe centred to the northeast in the Hudson Bay region. The continental ice flow direction, as measured by glacial striae in the Setting Net Lake area, varies between S60W and S65W. The map-area lies in the region that was covered by glacial Lake Agassiz during the retreat of the Wisconsin

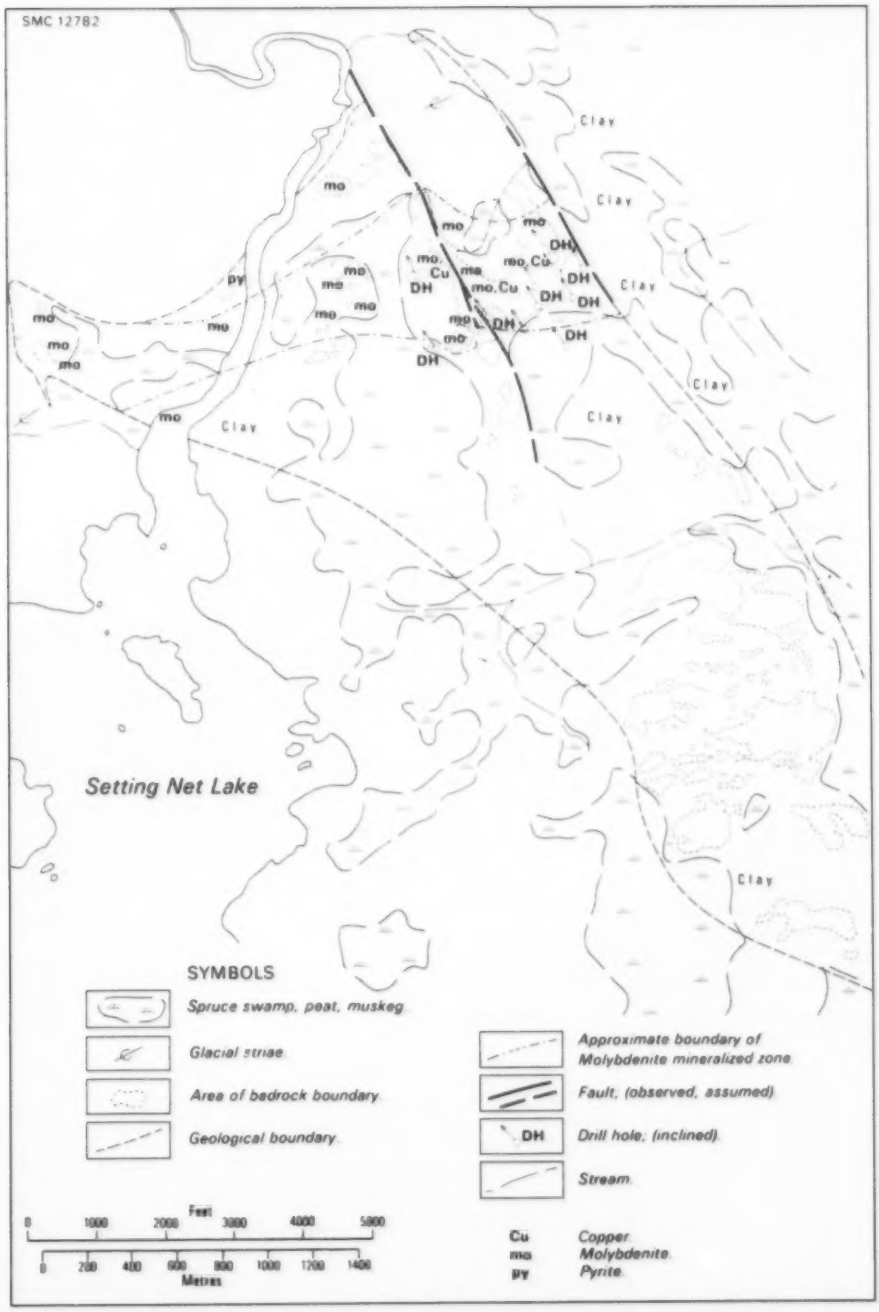

Figure 2 - Geological map of the Setting Net Lake pluton showing distribution of bedrock outcrop, the zone of molybdenite mineralization, deposits of Pleistocene clay and Recent peat-muskeg swamp. (Modified after Ayres 1960b).

ice front into northwestern Ontario and is partly covered by massive to varved, calcareous Pleistocene lake clays. These deposits of impermeable clay occupy basins in the pre-Agassiz topography and inhibit effectively the upward motion of groundwater from underlying till and bedrock sources. Local relief in the immediate vicinity of the Setting Net Lake stock is approximately 40 m (125 feet). Exposures of Wisconsin till and bare, wave-washed bedrock occur at the higher elevations and form windows in the surrounding lacustrine cover. The approximate areal distributions of swamp, clay and till deposits are shown in Figure 2.

The explored part of the mineralized zone is situated mainly on a thinly drift-covered bedrock rise that is surrounded by extensive poorly-drained spruce swamp and muskeg resting on clay deposits of variable thickness. Well differentiated podzolic soils are developed on the freely drained, sandy stone till that mantles the upland areas. The distribution of specific species of coniferous and mixed forest vegetation is strongly related to areal variations in soil drainage and type. Jack pine is abundant in areas of thinly moss-covered bedrock and freely drained sandy soil, and aspen and birch species occur mainly on well-drained, till-covered hillside slopes. Black spruce is widespread throughout the map-area, but is particularly dominant in poorly drained peat and muskeg environments. The region is located near the southern limit of the zone of discontinuous permafrost and is cool and dry with about 610 mm (24 inches) of precipitation per year and a mean annual temperature of -3°C (27°F).

ECONOMIC GEOLOGY AND MINERAL EXPLORATION

An extensive zone of molybdenite concentration has been outlined and described by Ayres (1968; 1969a,b) and Ayres and Averill (1971) in altered granodiorite and quartz monzonite at the north end of the Setting Net Lake stock. Within an east-trending mineralized zone that is up to 450 m (1,500 feet) wide and 2400 m (8,000 feet) long, widespread molybdenite has been found: (1) along the margins of narrow, variably spaced quartz veins filling joints in the stock, and (2) as minor disseminated mineralization throughout the granodiorite and quartz monzonite. The molybdenite-bearing zone was first reported by Ayres (1968) and was subsequently explored during 1969 by Asbestos Corporation (Explorations) Limited (now Minorex Limited) and Conwest Exploration Company Limited (under option from North Rock Explorations Limited, Alchib Developments Limited, and Flint Rock Mines Limited). The mineralization was evaluated by surface blasting and pitting and, at the east end of the zone, by 8 NX diamond drill holes. The boundaries of the main molybdenite-bearing zone and the locations of the drill holes are shown in Figure 2.

The molybdenite-bearing quartz veins have a relatively uniform trend of approximately N65E, dip steeply south, and are up to 15 cm (6 inches) wide, although most veins are less than 2.5 mm (1/10 inch) wide. The quartz veins are clearly visible on the weathered surfaces of outcrops, but molybdenite is generally observed only on freshly broken rock surfaces. The quartz veins pinch and swell and locally branch, but are in general traceable for long distances along strike. The veins are normally widely spaced but, in

certain highly mineralized parts of the stock, they are only 2.5 to 5 cm (1 to 2 inches) apart. Molybdenite seams along the margins of the veins measure generally only a fraction of a millimetre, but are locally up to 6 mm (¼ inch) wide. In areas of post-molybdenite shearing at the east end of the mineralized zone, the surfaces of molybdenite seams are covered by bright yellow ferrimolybdite oxidation. Average grade in 6 of the NX diamond drill holes is 0.06 percent MoS_2 (Assessment Files Research Office, files 2.904 and 63.2761, Ontario Division of Mines, Toronto).

Pyrite occurs in many of the veins and is also disseminated throughout the stock. The mineralized zone contains minor chalcopyrite which normally occupies north-trending fractures (Ayres 1969a) and is most abundant near faults, fractures and shear zones that appear to be younger than the molybdenite-bearing veins. Many minor occurrences of molybdenite in the metavolcanic country rocks may be linked genetically with the molybdenum-bearing granitic pluton. Ayres and Averill (1971) have emphasized the many obvious similarities between the mineralized Setting Net Lake stock and the molybdenite occurrences associated with Mesozoic and Cenozoic epizonal, porphyritic felsic plutons in British Columbia.

GEOCHEMICAL METHODS EMPLOYED

SAMPLING AND CHEMICAL ANALYSIS OF ROCKS, SOILS, AND VEGETATION

Patterns of widely spaced sampling of rocks, soils and vegetation were used to test surface geochemical and biogeochemical responses over the zone of low-grade molybdenite-pyrite-chalcopyrite mineralization in the north end of the Setting Net Lake pluton.

Rocks

At each of 50 outcrop sites within the boundaries of the pluton, two representative samples of unweathered rock chips weighing 0.9 to 1.36 kg (2 to 3 pounds) were collected about 6 to 15 m (20 to 50 feet) apart. The paired system of duplicate sampling is similar to the method outlined by Garrett (1971) and is used to compare local sampling variability at the outcrop level with overall chemical variability within the intrusion. The sampling was designed to determine patterns of primary metal dispersion in the plutonic rocks. Samples were, therefore, selected to provide representative coverage of the intrusion and to avoid contamination by vein and dike material as far as possible. After retaining a small chip for thin sectioning and reference, the 100 rock specimens were each successively passed through a jaw crusher and a cone crusher set to deliver material of about 1.68 mm (10 mesh) size. Crushed material was mixed by riffling on paper sheets and a sample split was taken for grinding to 74 micron (-200 mesh) size in a steel disc grinder. Previous studies indicated that the use of steel discs introduced insignificant levels of sample contamination for the principal trace elements sought (Cu, Mo, Pb, and Zn) and produced greatly increased speed and

efficiency in sample preparation. A separate sample split was used for the determination of mercury, and this material was hand ground to prevent Hg loss due to heating.

The rock powders were treated with hot HNO_3-HC1 leach, and the resulting solutions were diluted and aspirated for the determination of copper, zinc, lead, and manganese by atomic absorption spectrophotometry. Molybdenum was determined colorimetrically by a zinc dithiol technique, following a total decomposition of the powdered sample by a modified sodium carbonate fusion. The molybdenum content of the sample solution was determined by visual comparison with prepared standard molybdenum solutions.

A modification of the cold vapour atomic absorption method was used for the determination of mercury in rock samples. The method is summarized as follows: The sample is decomposed in HNO_3-HC1 (aqua regia) in the presence of potassium permanganate. Decomposition of sulphide minerals in aqua regia leads to loss of SO_2 at this stage, and the presence of a strong oxidizing agent ($KMnO_4$) prevents the formation of mercury (0) and loss of Hg in the gaseous state. After the sample is digested, a reducing agent (stannous chloride) is added prior to bubbling the sample gas through a closed system tube to a cell in the light path of an atomic absorption spectrometer. Absorption of the 2537A mercury emission line radiation by mercury (0) atoms is then measured against standard mercury solutions.

Sulphur was determined by a rapid combustion method using potassium iodate as a titrant for sulphur dioxide and starch iodide solution as an indicator. The weighed sample was burned in an oxygen atmosphere in a high temperature 'Leco' induction furnace and the liberated sulphur dioxide was iodometrically titrated.

Fifty samples (one from each outcrop site) were analysed for SiO_2, K_2O, and Na_2O in order to estimate variations in bulk rock composition within the pluton. Silica was determined by classical wet chemical gravimetric techniques and the alkalis were analysed by flame emission photometry.

Mineral Soils

Forty-four samples of 'B' horizon soil were collected at intervals of 122 m (400 feet) on a grid system covering the east end of the main zone of molybdenite mineralization. Picket lines spaced 122 m (400 feet) apart between 12W and 8E on baseline 3 (Figure 3) were used for control. Five samples were collected at control sites established near the east end of baseline 4 in an unmineralized area.

Soil samples were air dried and screened at a field base camp and the 177 micron (-80 mesh) sieve fraction was retained for analysis. Samples were analysed by atomic absorption spectrophotometry for hot HNO_3-HC1 leachable Cu, Zn, Pb, and Mn. Molybdenum was determined by the zinc dithiol method.

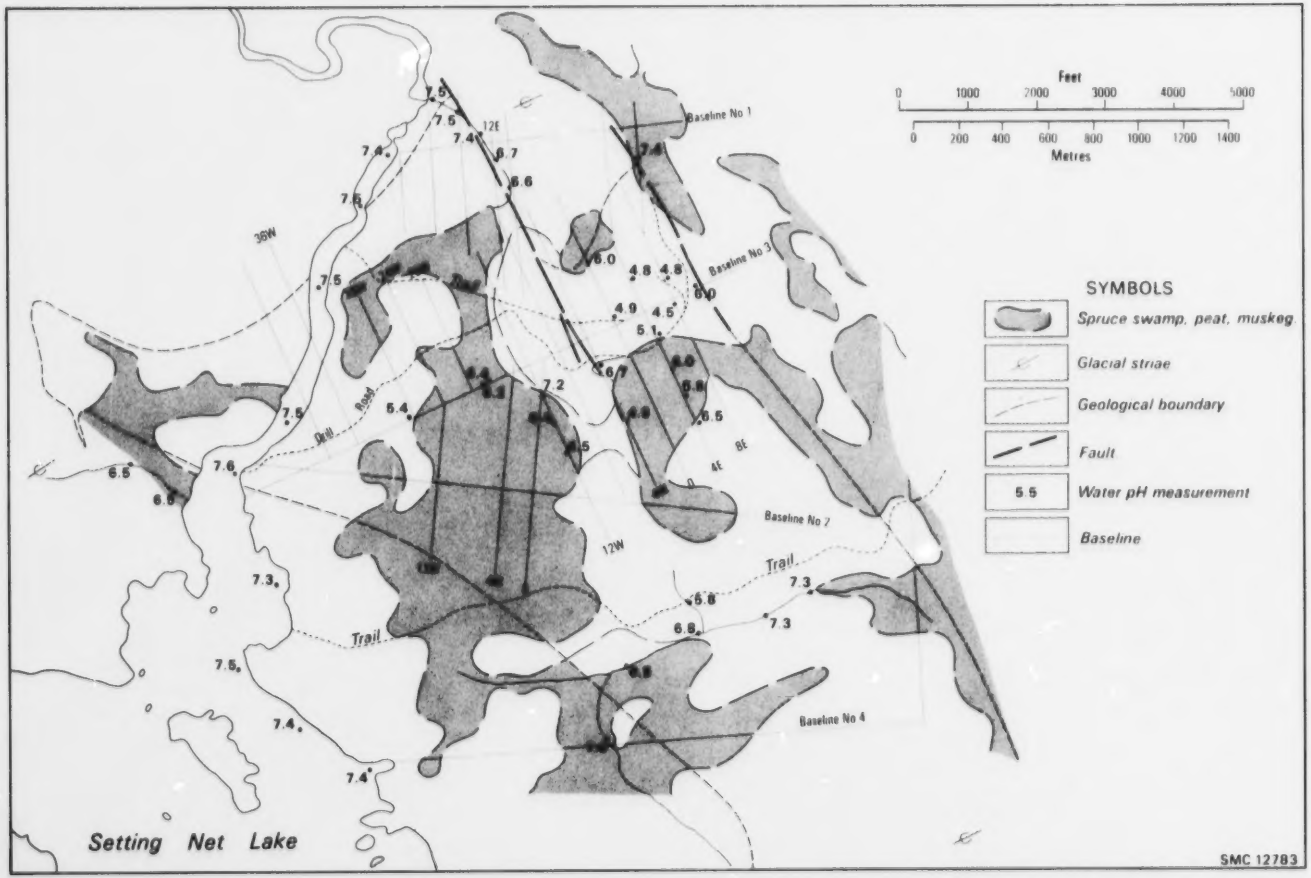

Figure 3 - Sketch map of north part of the Setting Net Lake pluton showing trails, roads, baselines and picket lines used for geochemical sampling control. Water pH measurements in soils and lake, stream and swamp water are also shown.

Vegetation

Samples of lower bark, second year twigs, and second year needles were collected from black spruce (*Picea mariana*) at 25 sites near known mineralization and in surrounding terrain covered by Pleistocene glacial lake clays. These sites were located at intervals of 122 m (400 feet) along baseline 3 between 12W and 16E (not shown in Fig.), and on picket lines 8W and 4E (Figure 3). Similar samples were collected from the 5 control sites over the barren southern part of the intrusion. At selected sites, samples of lower bark and second year twigs were also collected from jack pine (*Pinus banksiana*), trembling aspen (*Populus tremuloides*), and white birch (*Betula papyrifera*) for the purpose of comparing Mo and Cu responses in the various plant species. Only black spruce occurs in sufficient abundance and uniform density for routine sampling on a grid pattern.

At each station, a sample tree was selected and a soil sample was collected from the upper 'B' horizon near the base of the tree. The sample trees were chosen to maintain general uniformity of age and size. Previous studies by Wolfe and Wright (1970) and Hornbrook (1972) indicated that within broad limits, no significant correlations exist between age or physical measurements and the absolute concentration of metal elements in the sample trees. Samples of second year twigs, second year needles (in the case of coniferous species), and lower bark were collected and prepared for analysis. They were oven-dried for 12 hours. Then, accurately weighed samples of 20 to 25 grams of oven-dried material were ashed in a time-temperature controlled muffle furnace over a 10 hour cycle. The ash was weighed to calculate the ash per cent and used for the determination of Cu, Pb, Zn, Ni, Co, and Mn by atomic absorption spectrophotometry after HNO_3 decomposition. Molybdenum was determined colorimetrically by the zinc dithiol method. Analytical results used in this report are reported as parts per million of metal in ashed material.

An evaluation of the litho-, pedo-, and biogeochemical trace element data obtained during this study demonstrated that only molybdenum and copper produced anomalous halos related to the occurrence of known molybdenite mineralization in the northern part of the Setting Net Lake pluton. Although the other trace elements measured (Hg, Pb, Zn, Mn, Ni, Co) provide useful information for establishing background levels in the rocks, soils and vegetation of the area, only Mo and Cu are useful indicators of mineralization at this particular deposit. The remainder of this report is, therefore, devoted mainly to the discussion of patterns of Mo and Cu dispersion in the rocks, soils and vegetation surrounding the deposit.

DISCUSSION OF GEOCHEMICAL AND BIOGEOCHEMICAL RESULTS

ROCKS

Average metal abundances in the rocks of the intrusion were estimated by separately averaging trace metal data from 50 samples collected at 25 outcrops in the mineralized part of the stock, and 50 samples collected from 25

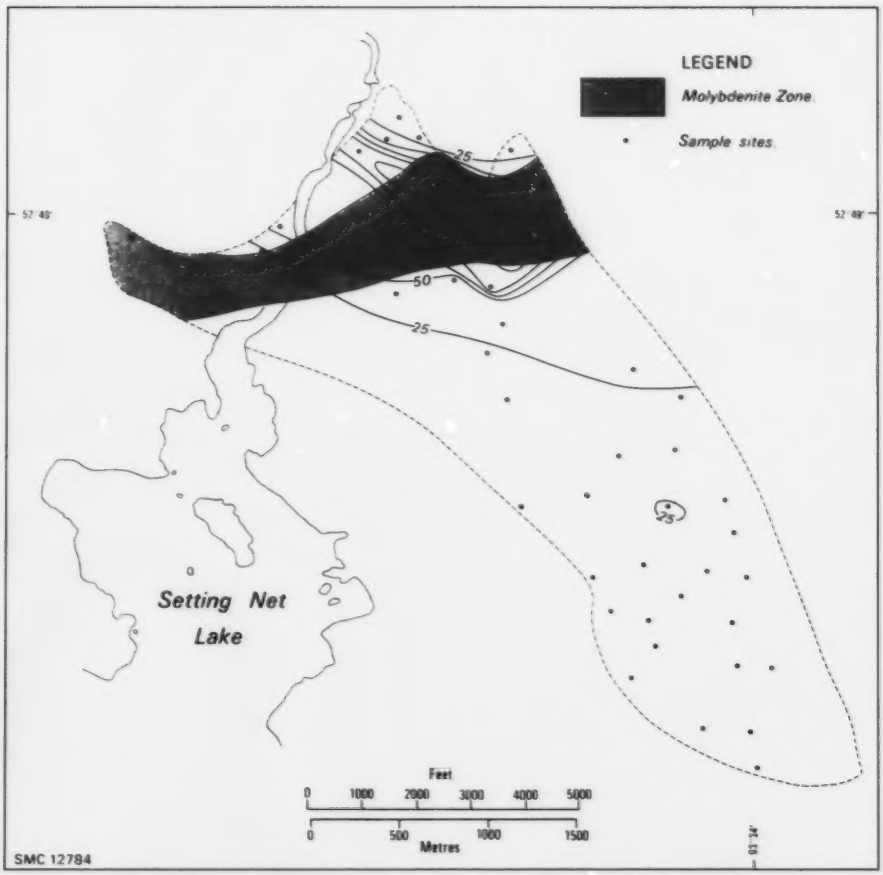

Figure 4 - Hot HNO_3-HCl soluble copper in plutonic rocks of the Setting Net Lake stock.

outcrops in the barren part of the stock. On this basis, the metal averages obtained were (in ppm): Cu-8, Mo-1.7, Zn-30, Mn-277 in the unmineralized south half, and Cu-61, Mo-26, Zn-30, Mn-240 in the mineralized north half of the stock. Copper and molybdenum are highly enriched in the granitic rocks that host the mineralized quartz veins, but zinc and manganese concentrations remain uniform throughout the pluton. Lead and mercury are present at levels below the limits of analytical detection (25 ppm Pb and 50 ppb Hg). It is also worth noting that copper and molybdenum abundances in the south half of the pluton are consistent with average background levels for granitic rocks and give no clue to the presence of molybdenite-pyrite-chalcopyrite-bearing plutonic rocks in the north half of the intrusion.

Patterns of copper and molybdenum distribution in rocks of the Setting Net Lake pluton are shown in Figures 4 and 5. Average values for two deter-

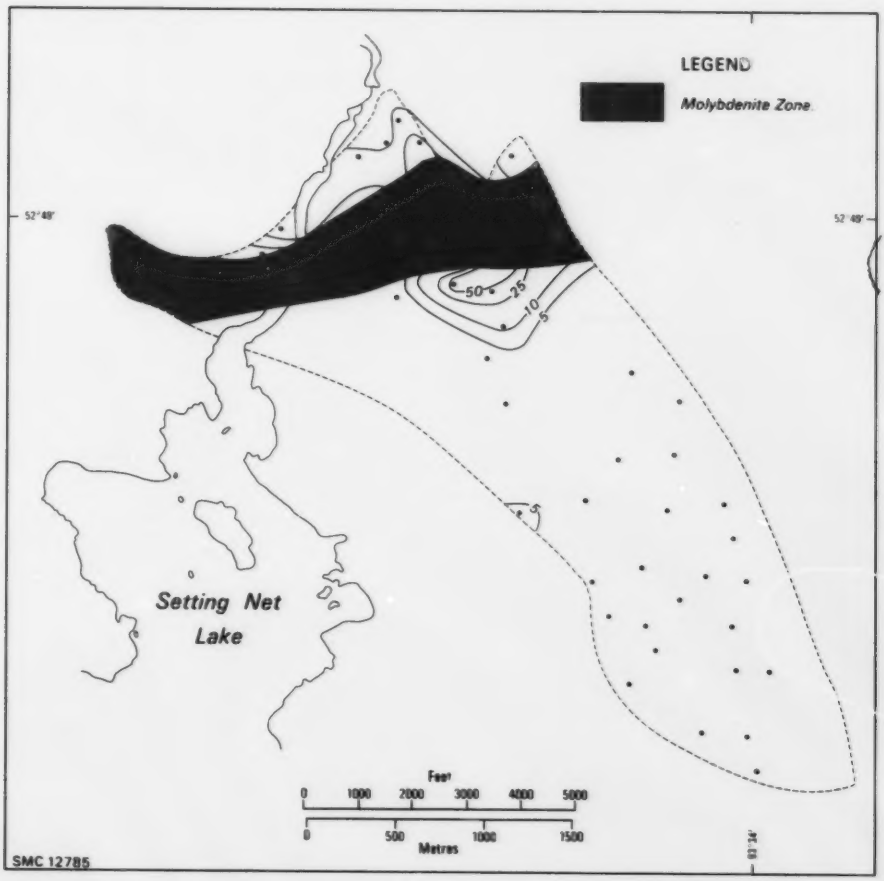

Figure 5 - **Total molybdenum in rocks of the Setting Net Lake stock. Contoured value at each site represents the average of two determinations on two separate samples.**

minations at each of the 50 outcrop sites were used to produce the contoured maps. The contoured maps clearly outline patterns of anomalously high copper and molybdenum values in the northeast part of the stock. In a general way, these trace element patterns outline the eastern half of the observed zone of mineralization (shown as a shaded zone) in Figures 4 and 5. However, the anomaly trends show some tendency toward a northwest elongation which is discordant to the east-west trend of the molybdenite zone. The overall configuration of the lithogeochemical patterns is substantially influenced by the paucity of outcrop in the northwest part of the intrusion. Nevertheless, there is some reason to believe that the mineralized zone may be arcuate or west-northwest trending and that it may extend beneath clay and muskeg cover southeast of the presently defined limits of molybdenite mineralization.

Variability of the major oxides SiO_2, Na_2O, and K_2O in the Setting Net Lake pluton was tested by analyzing 50 rock specimens chosen by random

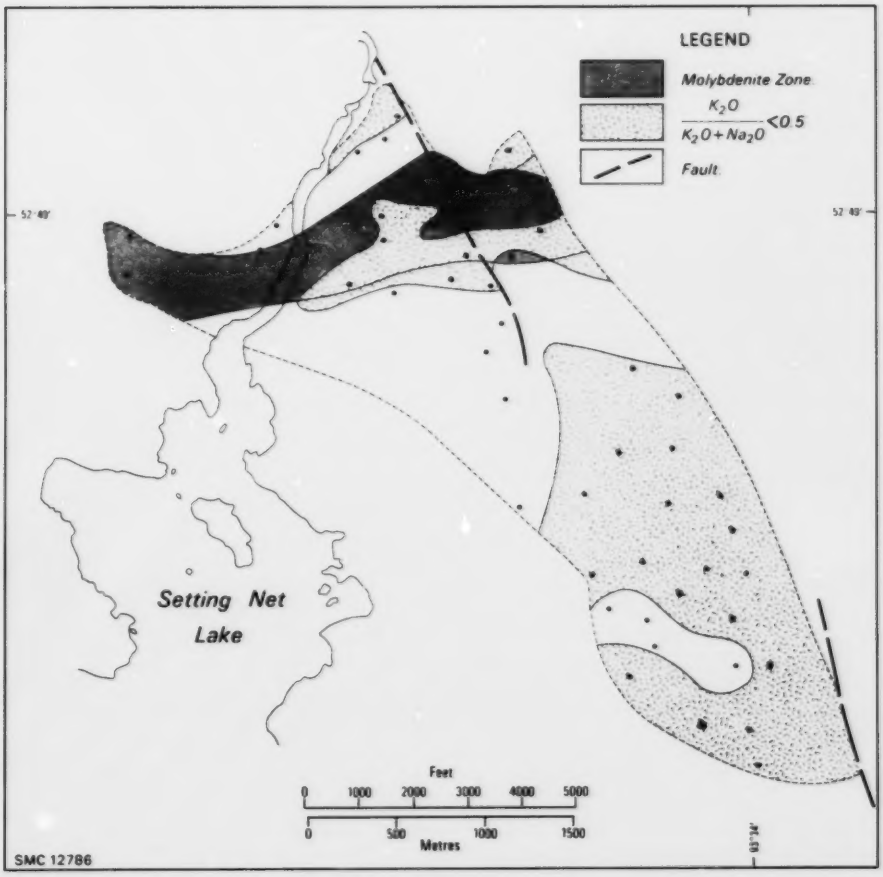

Figure 6 - Distribution of $K_2O/K_2O + Na_2O$ in plutonic rocks at 50 sites in the Setting Net Lake stock.

selection of one of the two samples collected at each of the 50 sites plotted in Figure 6. Average values followed by standard deviations are: SiO_2 - 70.77 ± 1.70, Na_2O - 3.97 ± 0.46, and K_2O - 3.95 ± 0.48 percent. Silica variation within the intrusion is small - 95 percent of the samples contain SiO_2 in the range 67.4 to 74.2 percent, and no statistically valid pattern of areal variation can be shown. The distributions of sodium and potassium reflected by the plot of K_2O/Na_2O ratios shown in Figure 6, suggest that the southeast and east-central parts of the pluton are lower in potassium relative to sodium than the west and northwest parts.

SOILS AND VEGETATION

Surface geochemical and biogeochemical responses to widespread molybdenite-pyrite-chalcopyrite mineralization under transported Quaternary cover have been studied at Setting Net Lake by comparing molybdenum and copper concentrations in samples of soil and vegetation from unmineralized and mineralized areas. The essential features of copper and molybdenum distribution in 'B' horizon soil and various types of ashed vegetation are demonstrated by data collected at 5 unmineralized sites and at 5 selected sites near the east end of the mineralized zone. These data are listed in Tables 1 and 2. The 5 unmineralized sites are located over barren granodiorite in the east-central part of the Setting Net Lake stock near the east end of baseline 4 (see Figure 3). Data collected from these sites are used to establish regional background metal content in soil and plant materials and to provide a basis for comparison with similar data collected near known mineralization in the northeastern part of the stock.

Anomaly definition in terms of size, intensity, and spatial relationship to known mineralization is the principal criterion used in estimating the relative effectiveness of the various geochemical and biogeochemical methods tested. Representative geochemical and biogeochemical data of the type shown in Tables 1 and 2 have been used to determine relative geochemical relief or anomaly contrast in the various sampled materials in the survey area. Relative metal abundances showing maximum contrast between background and anomaly peak are most desirable from the standpoint of anomaly interpretation.

The following principal observations are warranted after an examination and comparison of geochemical and biogeochemical responses at the Setting Net Lake Mo-Cu deposit.

1. Molybdenum concentrations range from 1 ppm to 80 ppm in 'B' horizon soils. In background areas, soil developed on glacial till over unmineralized granodiorite and quartz monzonite contains a uniform 1 ppm Mo.

2. Molybdenum concentrations range from 2 ppm to 71 ppm in the ash of second year black spruce needles. Background values range from 2 to 4 ppm.

3. Molybdenum concentrations range from 4 ppm to 34 ppm in the ash of second year black spruce twigs. Background levels range from 4 to 5 ppm.

4. Molybdenum concentrations range from 2 ppm to 4 ppm in the ash of black spruce lower bark with no significant variation between background and anomalous areas. Samples of black spruce bark clearly do not reflect changes in the Mo content of supporting soils.

Table 1 | Molybdenum content of soils and ashed vegetation at selected anomalous and background sites over Setting Net Lake pluton. All values in ppm.

Site No.	'B' Horizon Soils	Black Spruce			Jack Pine	
		Lower Bark	2nd Year Twigs	2nd Year Needles	Lower Bark	2nd Year Twigs
Anomalously High Group						
29	12	4	23	21	19	27
32	4	3	15	23	13	28
33	80	4	5	29	16	32
22	50	3	14	31	6	8
41	60	3	34	71	22	52
Background Group						
45	1	4	5	4	6	8
46	1	3	5	4	5	7
47	1	2	5	3	7	6
48	1	3	5	3	9	6
49	1	2	4	4	7	6
Anomaly Contrast						
	80	1	7	20	3	8

Table 2 | Copper content of soils and ashed vegetation at selected anomalous and background sites over the Setting Net Lake pluton. All values in ppm.

Site No.	'B'Horizon Soils	Black Spruce			Jack Pine	
		Lower Bark	2nd Year Twigs	2nd Year Needles	Lower Bark	2nd Year Twigs
Anomalously High Group						
29	33	46	158	50	84	190
32	92	83	251	110	76	145
33	311	49	250	186	202	345
22	23	71	275	78	137	307
41	156	44	250	133	129	246
Background Group						
45	7	120	321	75	151	300
46	6	93	259	70	94	230
47	15	33	303	63	180	223
48	6	77	275	42	149	237
49	8	60	211	66	112	258
Anomaly Contrast						
	37	1	1	3	1	1

5. Molybdenum concentrations range from 6 ppm to 52 ppm in the ash of second year jack pine twigs. Background levels range from 6 to 8 ppm.

6. Molybdenum concentrations range from 5 ppm to 22 ppm in the jack pine lower bark. Background values range from 5 to 9 ppm.

7. In every case except one, absolute levels of molybdenum are higher in jack pine than in comparable black spruce samples collected at the same site.

8. Copper concentrations range from 3 ppm to 311 ppm in 'B' horizon soils. Soils developed on glacial till over unmineralized granodiorite and quartz monzonite contain 3 to 15 ppm Cu. Threshold and anomalous levels are 20 ppm and 40 ppm respectevely.

9. Copper concentrations range from 32 ppm to 322 ppm in the ash of second year black spruce needles. Threshold and anomalous levels are 75 ppm and 100 ppm respectively.

10. Samples of lower bark and second year twigs from black spruce and jack pine species do not adequately reflect variations in the Cu content of supporting soils and show no significant differences in Cu between background and anomalous areas.

The above observations combined with geochemical and biogeochemical anomaly maps (Figures 7 and 8), showing patterns of metal variation in relation to known mineralized rocks, form the basis for selecting (1) molybdenum analysis of 'B' horizon soil, (2) copper analysis of 'B' horizon soils, and (3) molybdenum analysis of second year spruce needle ash, as the most useful methods for exploring low-grade mineralization of the Setting Net Lake type. In terms of cost, reliability and anomaly contrast, soil geochemistry will normally be more useful than biogeochemistry in locating buried mineralization in regions of thin transported cover. However, in widespread regions of peat and muskeg terrain where near-surface mineral soils are absent, analysis of ashed second year needles from black spruce may produce effective results.

Timperley and others (1972) have observed that metal concentrations in vegetation are determined by (1) metal concentrations in the supporting soil or soil solution, and (2) the specific biochemical requirement of a plant for a given metal. These two variables operate independently to produce a net result for each specific metal in each plant species. To be useful in mineral exploration, the metal content of a sample of plant material must bear a fairly simple relationship to the metal content of the underlying soil or bedrock environment. The content of metal in plant ash as a function of soil metal concentration seldom approaches a one-to-one relationship: in the Setting Net Lake case, only the Mo content of spruce needle ash shows a

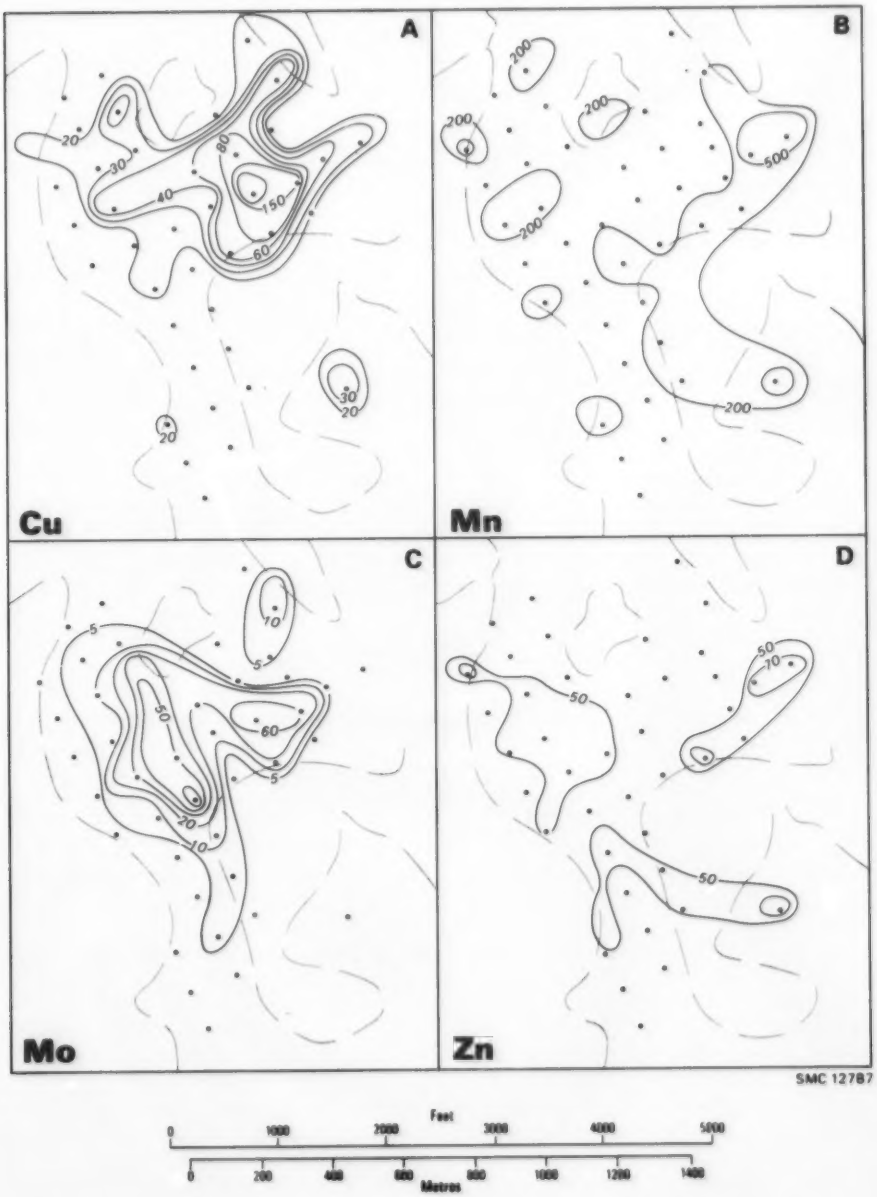

Figure 7 - **Geochemical anomaly maps showing the distributions of Cu, Mn, Mo, and Zn in 'B' horizon soil over the east end of the molybdenite-bearing zone in the north end of the Setting Net Lake pluton.**

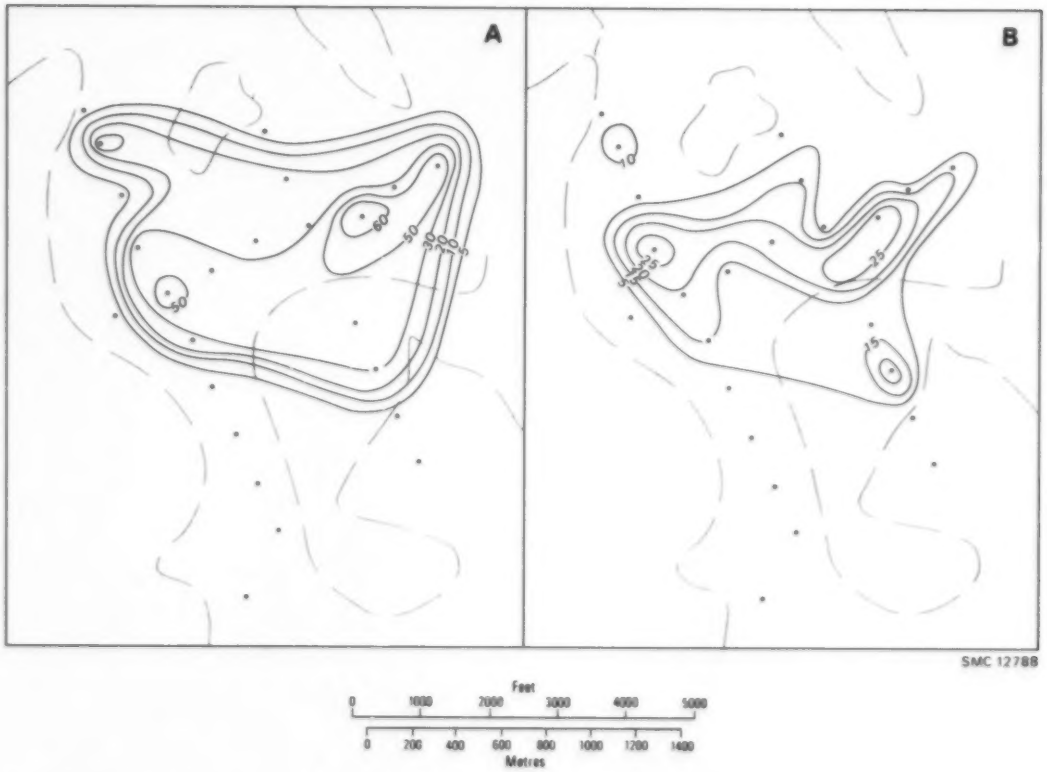

Figure 8 - **Biogeochemical anomaly maps showing the distribution of: (A) molybdenum in black spruce second year needle ash, and (B) molybdenum in black spruce second year twigs.**

reasonable correspondence with Mo concentration in supporting soils. The general lack of correspondence between plant composition and underlying soil or soil moisture composition is attributable to processes of biochemical accumulation and exclusion that are determined by the plant's specific requirement for a metal.

Certain plant species show a remarkable ability to selectively concentrate specific metals from supporting soils of average background composition; other species appear capable of selectively excluding certain metals keeping the content below a limited threshold. For purposes of mineral exploration, extraordinary metal accumulation is less important than the accumulation ratio or anomaly contrast as expressed by the ratio of anomaly peak to average background. Such accumulation may not be useful, if relative abundances of elements in the soil are not accurately reflected by accumulation in the plant.

Copper and molybdenum contents give a typical example of diverse metal uptake behaviour in coniferous species (Wolfe 1971), and this fact is well illustrated by the data shown in Tables 1 and 2. A comparison of copper and molybdenum values in the needles of black spruce and in supporting soils of background and anomalously high areas shows molybdenum contrast in plant ash ranging as high as 20 to 1; copper contrast is limited to 3 to 1 in vegetation growing in soil containing as much as 30 times background levels of copper. Similar copper-molybdenum uptake behaviour has been reported in alpine fir (Hornbrook 1969; 1970) and in balsam fir (Canney 1970; 1971) over large, low-grade copper-molybdenum deposits in west-central British Columbia and west-central Maine. In each case, substantial 10- to 100-fold increases in the copper concentration of soils are typically associated with very restricted 2- to 3-fold increases in the copper content of ashed twigs from coniferous species growing on these soils. It seems quite clear from these surveys that the copper content of the plant ash is determined partly by the concentration of copper in the supporting soil but mainly by the specific requirements of the plant for this metal. In comparison, the molybdenum content of coniferous twigs and needles is determined mainly by the concentration of this metal in the soil and only to a lesser extent by some other biochemical requirement.

SECONDARY DISPERSION OF COPPER AND MOLYBDENUM

Although certain plant species have a limited ability to break down primary minerals and extract elements, biogeochemistry normally detects only metals capable of moving in solution. Metal concentrations in the underlying soil must, therefore, exist in a form that is immediately available for uptake by the root systems, generally in the ionic state in aqueous solution or in readily exchangeable form on the surfaces of soil clay minerals. As a result, biogeochemical responses are closely related to variables such as soil pH, Eh, exchange capacity and complexing agents that control metal mobility in the surface environment.

Secondary chemical dispersion from mineralized subcrop is achieved by

solution, transport and precipitation processes that are largely controlled by Eh-pH dependent reactions in oxidizing metal sulphide systems.

$$Cu_2S^{+1} + 2H_2O = CuS^{+2} + Cu(OH)_2^{+2} + 2H^+ + 2e^-$$
$$CuS^{-2} + 2H_2O = Cu(OH)_2 + S^O + 2H^+ + 2e^-$$

Sulphide oxidation reactions of this type are hydrogen ion producing reactions and, therefore, are pH dependent at a given equilibrium condition. The Eh-pH diagram for the $Cu\text{-}H_20\text{-}CO_2\text{-}0_2\text{-}S$ system at 25°C and 1 atmosphere pressure (Figure 9) gives example of the general form of solubility relationships for a large number of ore-associated metals. Although the field of metal solubility may expand or contract according to individual cation activities, most ore metal compounds (including Cu, Pb, Zn, Ni, Co, Fe and Mn) are soluble in the oxidized-acidic environment. General relationships of this type have important implications in Precambrian terrain where potential ore subcrops are isolated from the oxygenated surface weathering environment by thick accumulations of impermeable Pleistocene clay (Hansuld 1966; Wolfe 1971). The subsurface alkaline-reducing environment commonly associated with Pleistocene calcareous clays limits the solubilities of ore-metal sulphide minerals (including copper) so that primary sulphide minerals at bedrock surfaces overlain by these clays remain essentially unaltered.

The general solubility relationships that apply in most ore-metal sulphide systems differ significantly in the case of molybdenum. Unlike Cu, Zn, Ni, etc. which exist to a large degree as simple bivalent cations in aqueous solution, Mo forms a soluble molybdate $(Mo0_4)^{-2}$ complex anion in alkaline aqueous solutions. The stability fields indicated by Eh-pH reactions in the $Mo\text{-}Fe\text{-}S\text{-}H_20$ system at 25°C and 1 atmosphere (Figure 10) show that molybdenum is soluble and, therefore, mobile) in the molybdate form under oxidizing-alkaline conditions but remains insoluble as bright-yellow ferromolybdite at pH values less than about 6.0. Mo is, therefore, soluble and mobile at pH conditions where Cu and many other elements are insoluble.

These theoretical relationships are useful in explaining patterns of geochemical dispersion in soils and vegetation near the Setting Net Lake molybdenum-copper deposit. The explored zone of molybdenite-pyrite-chalcopyrite mineralization occurs mainly on a thinly till-covered, well-drained topographic high surrounded by extensive poorly-drained spruce swamp and muskeg resting on deposits of massive Pleistocene clay which effectively restrict the upward movement of groundwater from underlying till and bedrock sources. Within a relatively limited area, soil pH ranges from 4.5 near oxidizing sulphides to 7.5 over calcareous Pleistocene clays (Figure 2). The pattern of anomalous molybdenum in 'B' horizon soil (Figure 7c) is restricted to bedrock-glacial till 'windows' in the clay-swamp cover because: (1) soil samples are difficult to obtain in areas of thick organic accumulation and (2) molybdenum is not precipitated in the alkaline soils developed on clay deposits.

The pattern of anomalous molybdenum in second year black spruce needles (Figure 8a) extends into both the clay and swamp environments and is more widespread and sharply defined than the corresponding soil anomaly.

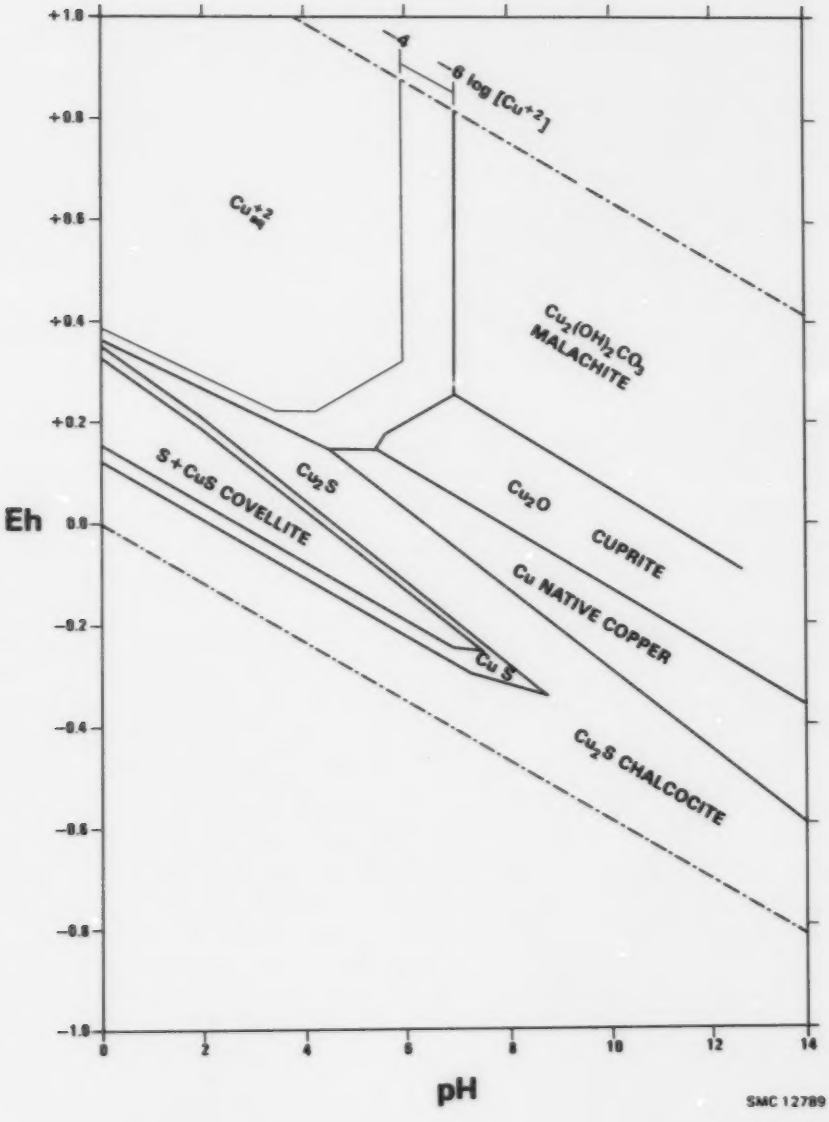

Figure 9 - Eh-pH stability fields in the Cu - H_2O - CO_2 - O_2 - S system at 25°C and 1 atmosphere pressure.

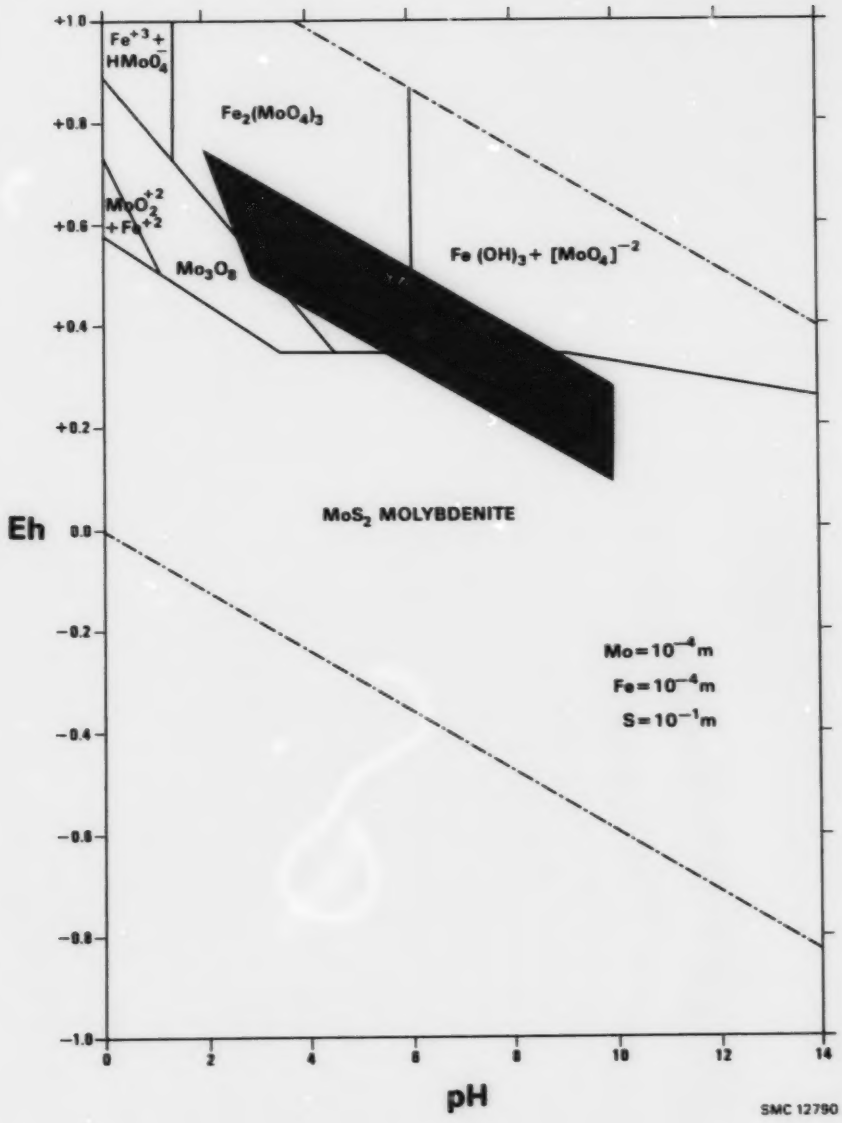

Figure 10 – Eh-pH stability fields in the Mo - Fe - S - H_2O - O_2 system at 25°C and 1 atmosphere pressure (after Baraksо and Bradshaw 1971).

The molybdenum content of vegetation may be regarded as an indirect indicator of Mo levels in soil solutions, and the existence of anomalous Mo in trees growing in alkaline soil environments confirms pH solubility relationships which predict increased solubility (i.e. mobility) of the molybdate ion with increasing pH. However, the extension of molybdenum biogeochemical anomalies into areas of clay and peat-muskeg cover probably reflects lateral transport of molybdenum-bearing surface run-off from upland areas. Vertical migration of molybdenum-bearing groundwater through impermeable clay beds and penetration of massive clay deposits by spruce root systems both appear to be unlikely possibilities.

The pattern of anomalous copper distribution in 'B' horizon soil (Figure 7a) is strongly localized near the main site of drilled mineralization between 5E and 8E on the baseline. Anomalous copper values extending eastward into areas of high pH soils developed on clay apparently reflect precipitation of laterally transported copper in the high pH environment.

Copper and molybdenum anomaly patterns must be explained in terms of pH-solubility relationships which can vary widely in diverse Eh-pH environments. Over much of the Precambrian Shield, the scale of these environmental domains may be relatively local and may severely limit the secondary dispersion of metals. Geochemical processes operating in these local environmental domains may, therefore, severely limit the application of regional geochemical exploration techniques in terrain similar to the Setting Net Lake area.

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